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Twinned Crystals of ,Poly(bis-p-fluorophenoxy)  
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# TWINNED CRYSTALS OF POLY[BIS(P-FLUOROPHOXY)PHOSPHAZENE]- PB(4-F)PP

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## ABSTRACT

Poly[bis(p-fluorophenoxy)phosphazene]-PB(4-F)PP crystals have been grown from dilute xylene solution. After heating above the thermotropic transition temperature, T(1) and then cooling to room temperature the specimens were examined by electron microscopy. Crystals initially prepared from solution are monoclinic, but then transform to a pseudohexagonal form above the T(1). Upon cooling down to room temperature this phase changes to an orthorhombic modification where the PB(4-F)PP crystals exhibit 60° rotational symmetry.

**Keywords:** Solution grown crystals, twinning, thermotropic transitions, polymorphism.

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Several polymorphic forms have been established for semicrystalline polyphosphazenes that exhibit thermotropic behavior<sup>(1-5)</sup>. For instance, poly[bis(phenoxy)phosphazene]-PBPP shows two polymorphic forms ( $\alpha$ - and  $\gamma$ -forms) and one mesoform ( $\delta$ -form) depending upon the crystallization conditions<sup>(4,5)</sup>. Whenever PBPP crystallizes to the 3D orthorhombic  $\gamma$ -form crystals from the thermotropic state, the crystallographic relationship between the  $\delta$ -form and the  $\gamma$ -form crystals has been established<sup>(4)</sup>. The  $[100]_{\delta}$  and the  $[100]_{\gamma}$  directions are essentially common features. The formation of (310) twinned crystals for the  $\gamma$ -form PBPP has been reported<sup>(6)</sup>. Such twinning appears to be a common feature in polyphosphazenes displaying thermotropic and polymorphic properties<sup>(1,3,6)</sup>.

This note describes the formation of twinned crystals in yet another polyphosphazene, PB(4-F)PP, obtained through cooling from the thermotropic state ( $T(1) \leq T \leq T_m$ ) to room temperature. Initially solution grown PB(4-F)PP crystals were prepared by isothermal crystallization from dilute xylene solution (<0.05% w/w) at 108°C (20 hr). These monoclinic crystals (designated as the  $\alpha$ -form) have unit cell dimensions  $a=2.64$  nm,  $b=1.92$  nm,  $c=0.491$  nm,  $\gamma=86^\circ$ , crystals<sup>(7)</sup> of the same structure with  $a=1.89$  nm,  $b=1.32$  nm,  $c=0.490$  nm and  $\gamma=77^\circ$  have also been reported.<sup>(8)</sup> PB(4-F)PP crystals undergo a transformation to a thermotropic pseudohexagonal phase ( $\delta$ ) at about 169 °C (determined by DSC measurements). upon cooling PB(4-F)PP at 2°C/minute to the room temperature from above the  $T(1)$  (for example from 200°C), a 2D pseudohexagonal disordered phase forms giving rise to a 3D crystal structure, which is orthorhombic in form. An electron micrograph of the heat treated (cycled) PB(4-F)PP crystals is presented in Figure 1(a) along with diffraction pattern obtained at 200 kV (Figure 1(b)). Figure 1(a) shows an intricate pattern of rod-like materials, hexagonally disposed with respect to each other.

A similar texture has been established for another polyphosphazene, poly[bis(trifluoroethoxy)phosphazene]-PBFP, prepared from THF solution<sup>(1,3)</sup>. The structural transformation conversion,  $\delta \rightarrow \gamma$ , also occurs in PBFP by heat treatment, with the  $[100]_\delta$  direction is parallel to the  $[100]_\gamma$  direction. These structural changes parallel those reported in PBPP crystals<sup>(4)</sup>. The pattern of behavior seems to be common to all polyphosphazenes that becomes disordered at the thermotropic transition where they pass into a chain extended 2D  $\delta$ -phase. The hexagonal symmetry has unit cell dimensions  $a=2.73$  nm,  $b=1.95$  nm from electron diffraction (see Figure 1(b)). Here the  $a^*$  axis and  $b^*$  axis are at right angles, suggesting the formation of an orthorhombic structure patterned after that found in the heating/cooling cycles also used for PBFP and PBPP crystals. The  $a^*b^*$  reciprocal net (drawn with thicker lines for the orthogonal form) in Figure 2 is displayed. The nets with thinner lines show a  $\pm 60^\circ$  inter-relationship, i.e.  $60^\circ$  rotational twinning. These hexagonally connected rod-like crystals in Figure 1(a) correspond to the  $[100]_\gamma$  direction for each composite crystal of twins. This morphology also coincides with the  $[100]_\delta$  direction since  $[100]_\delta$  is coincident with  $[100]_\gamma$ .

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FIGURE LEGENDS

Figure 1: (a) Electron micrograph of PB(4-F)PP crystals prepared from dilute xylene solution (0.01 % w/w) followed by heating at 200°C (30 minutes), and subsequent cooled to room temperature at a rate of 2°C/min and  
(b) is its electron diffraction pattern.

Figure 2: Reciprocal lattice net from the electron diffraction pattern of Figure 1(b) showing the  $a^*b^*$  60° relationship that exists in twinned crystals of PB(4-F)PP.

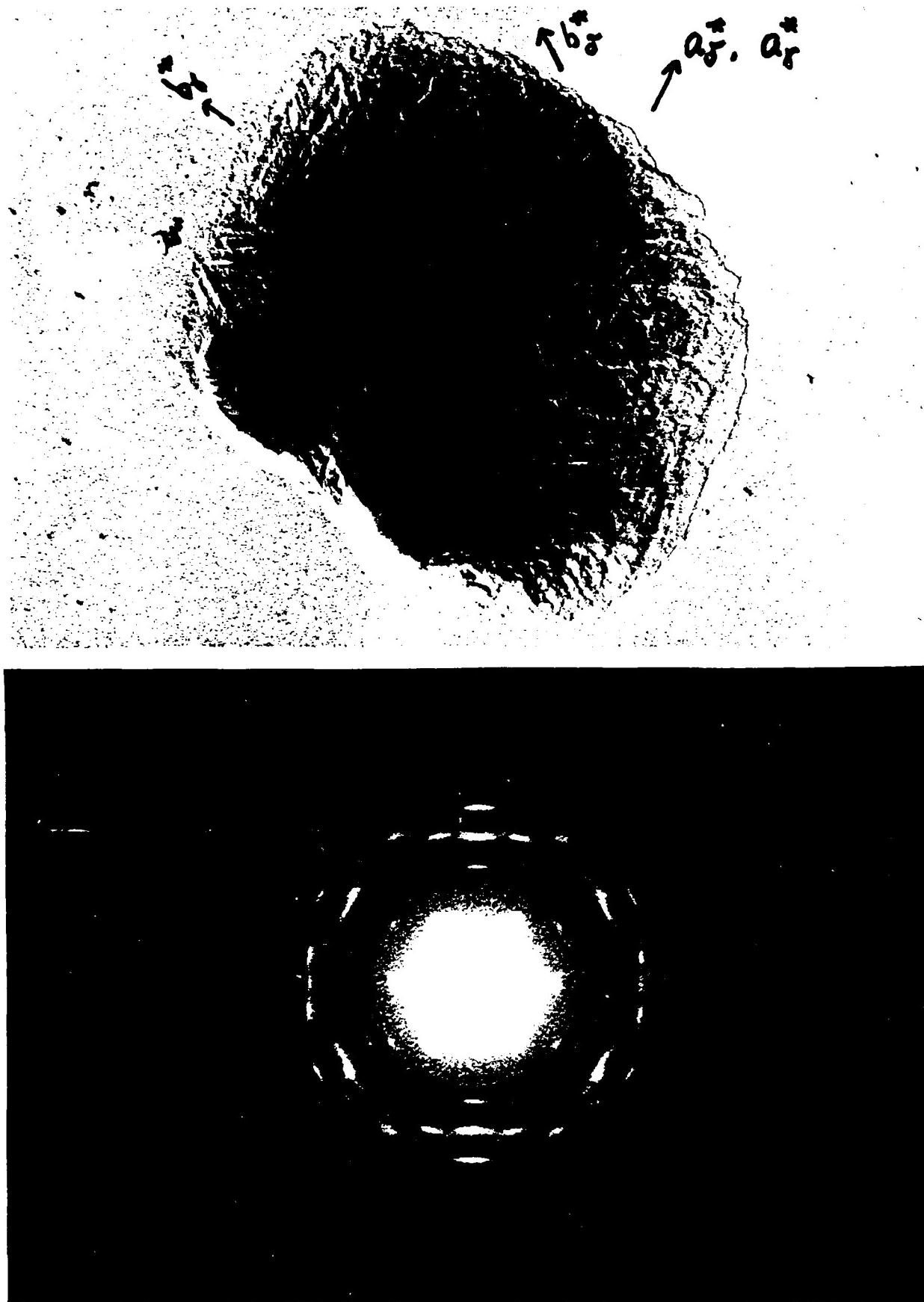


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(b) electron diffraction pattern

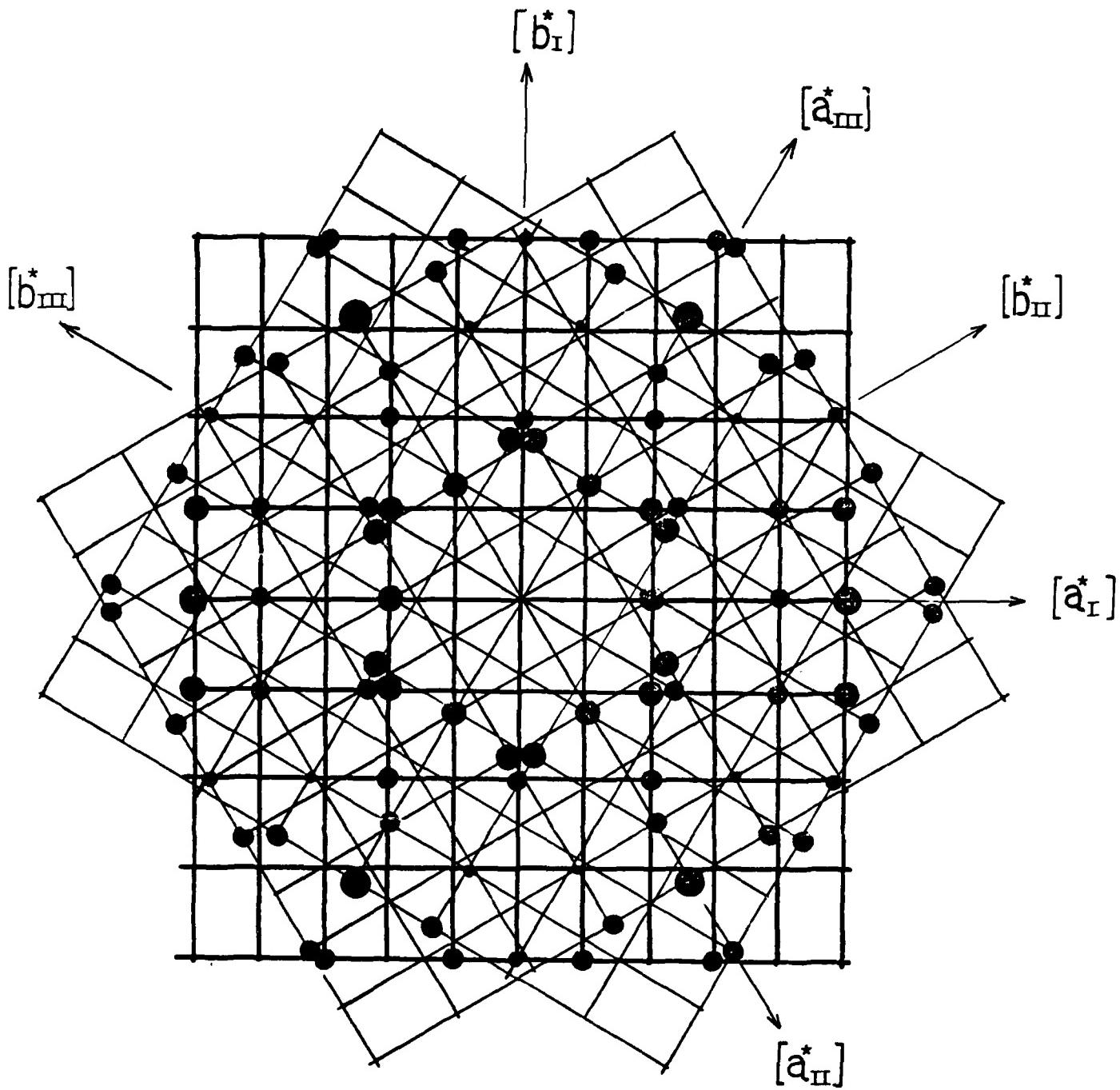


Figure 2: Reciprocal lattice net from the electron diffraction pattern of Figure 1(b) showing the  $a^*b^*$   $60^\circ$  relationship that exists in twinned crystals of PB(4-F)PP.

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